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# AN ANOMALOUS MAGNETIC BEHAVIOUR OF $K_3Cr_2(C_4O_3)$ $3H_2O$, STUDIED BETWEEN ROOM TEMPERATURE AND LIQUID OXYGEN TEMPERATURE

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The magnetic anisotropy and susceptibility measurements of $(NH_4)_3Cr(C_2O_4)_3$ $3H_2O$, assuming the salt to be monoclinic (Groth 1910), were made at room temperature and liquid oxygen temperature only by Krishnan, *et al* (1939). The $K_3Cr(C_2O_4)_33H_2O$ salt supposedly isomorphous with the ammonium salt was further investigated by Datta Roy (1958) over the whole liquid oxygen range. But the X-ray data of Nickerk and Schoening (1952) show that these salts are not only not isomorphous, but the ammonium salt belongs to the triclinic space group $P\bar{1}$, with two formula units in a cell, while the potassium salt is of monoclinic space group $P2_{1c}-C_{2h}{}^5$, with four formula units in a cell, so that the earlier identifications of the crystallographic axes were not correct, and consequently fresh measurements should be made to reassess the magnetic behaviour of these salts. The triclinic ammonium salt being more difficult to treat (Krishnan and Mukherji 1936, 1938; Ghosh and Mitra 1964; Ghosh 1966), as a first attempt we chose the monoclinic potassium salt. As the salt under investigation has feeble anisotropy, the single crystals were cut to nearly a square horizontal cross sections, to remove anisotropy of shape, about the axes of suspension. The suspension was made with a very fine quartz fibre and the entire suspension system was made as light as possible. The measurement was carried out in a very sensitive and accurate type of magnetic anisotropy balance and gas flow type cryostat set up in this laboratory by Ghosh and Mukhopadhyay (1966).

When the crystal was suspended with *b*-axis vertical to the magnetic field, the anisotropy in the horizontal plane *i.e.* $(\chi_1-\chi_2)$ increased as the temperature was lowered and at liquid oxygen temperature anisotropy became nearly ten times that of the room temperature value (Fig. 1a). The setting direction, i.e., the angle $\theta$ between *a*- and $\chi_2$-axis which is 63° at room temperature was found to change by 8° over the entire liquid oxygen range.

With the *a*-axis of the crystal vertical, *b*-axis setting normal to the magnetic field, a very peculiar phenomenon was observed as the temperature was lowered. From $\sim$220°K the crystal began to show a small change in the setting direction by a few degrees (Fig. 2c). Near 155°K the change was found to be very rapid, amounting to $\sim 65°$ for a temperature change of a few degrees and then again gradual. Since $b$-axis lying in the horizontal plane for this mode of suspension

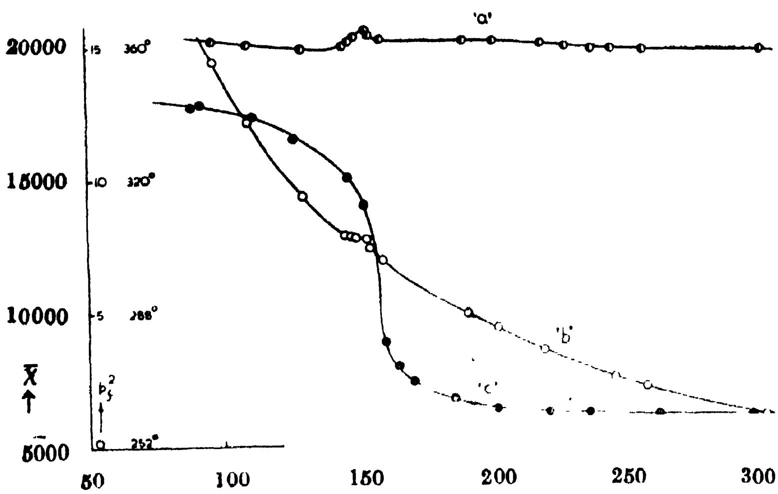


Fig. 1. half-filled circles —$(\chi_1-\chi_2)$
hollow circles—$(\chi_1-\chi_3)$
filled circles—$(\chi_3-\chi_2)$

is by crystal symmetry a fixed one, this large change is quite unusual. Secondly, the anisotropy in the plane normal to $a$-axis was found to be decreasing with the lowering of temperature and became zero at $\sim$153°K and then changed sign consistent with the large ($\sim$90°) change in the orientation of the original $b$-axis. With further lowering of temperature, the anisotropy increased again. The crystalline anisotropy $(\chi_1-\chi_3)$ as obtained from the above mentioned measurements was found to be increasing at first with the lowering of temperature but close to 155°K the curve of $(\chi_1-\chi_3)$ versus $T$ showed an inflexion and then increased again smoothly (Fig. . 1b). $(\chi_3-\chi_2)$ as obtained by subtracting the two anisotropies $(\chi_1-\chi_3)$ and $(\chi_1-\chi_2)$ was found to be very small at room temperature, and remained almost constant with the lowering of temperature upto $\sim$150°K. With further decrease of temperature $(\chi_3-\chi_2)$ increased slightly (Fig. 1c).

From the mean susceptibility measurement of this complex it was found that with the lowering of temperature the susceptibility increased normally but nearly at 153°K the value remained almost constant over a temperature range of $\sim$5°K and then again increased (Fig. 2b). In the corresponding mean moment square $p_f^2$ curve (Fig. 2a) a hump was observed at $\sim$220°K and a sharp maximum at $\sim$153°K, then $p_f^2$ value dropped nearly to the room temperature value and then increased again slightly as the oxygen temperature was reached.

Thus we may surmise that this anomalous behaviour in anisotropy and susceptibility is due to some transition in the crystal. The change in the setting direction with $\chi_3$—axis in the horizontal plane also supports this view. The 90°

change in the orientation of $\chi_3$ axis within a small interval of temperature indicates that this principal magnetic axis no longer coincides with the *b*-axis,

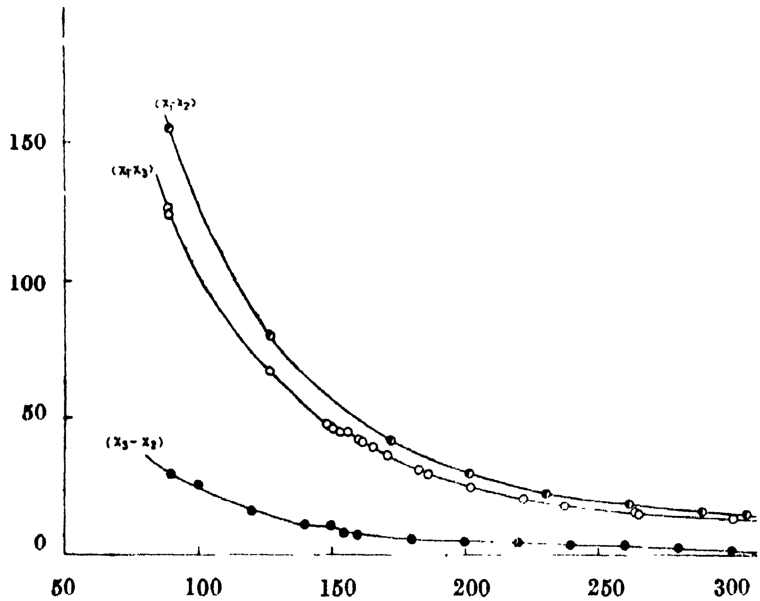


Fig. 2. half-filled circles —$p_f^2$—curve.
hollow circles —$\overline{\chi} \times 10^{-6}$
filled circles—change of setting angle with temperature.

thus destroying the condition of uniqueness of this axis in a monoclinic crystal. Thus the transi tion appears to be connected with a change in the crystal system. For getting more details of the transition we have undertaken X-ray and spectroscopic measure- ments of the salt.

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